

Field-induced disorder in a gapped spin system with non-magnetic impurities

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We study $S = \frac{1}{2}$ dimers which are weakly coupled by three-dimensional antiferromagnetic interactions J' . It is commonly known that doping with non-magnetic impurities immediately induces a long-range Néel order. We show that application of an external magnetic field H may drive the system back to a disordered phase. We discuss the zero temperature phase diagram in the (H, J') plane and we propose suggestions for experiments.

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In the last decade, much attention has been paid to the physics of gapped spin systems doped with non-magnetic impurities. Typical examples include $S = \frac{1}{2}$ ladders [1, 2, 3, 4, 5], $S = \frac{1}{2}$ dimerized chains [6], Haldane spin chains [7, 8], various two-dimensionally coupled systems [9, 10, 11, 12] and systems of $S = \frac{1}{2}$ dimers weakly coupled by three-dimensional (3D) interaction [13, 14]. It was shown [1, 4, 9] that the presence of impurities induces the formation of a gapless continuum of low-lying states within the gap, which leads to long-range Néel ordering in the presence of arbitrarily small 3D interactions.

On the other hand, considerable interest has been devoted to the behavior of gapped spin systems in strong magnetic fields. When the field is strong enough to close the spectral gap, the system enters a new phase. In absence of anisotropy, this new phase is critical in the purely one-dimensional (1D) case and exhibits long-range order in the presence of a weak 3D coupling. Experimentally, field-induced ordering has been studied for several substances, one of the better understood examples being the dimer material TiCuCl_3 [15, 16, 17, 18].

Consider an interacting 3D system of spin- $\frac{1}{2}$ dimers described by the following Hamiltonian:

$$\begin{aligned} \mathcal{H} = & J \sum_{\mathbf{r}} \mathbf{S}_{\mathbf{r},1} \cdot \mathbf{S}_{\mathbf{r},2} - H \sum_{\mathbf{r}\sigma} S_{\mathbf{r},\sigma}^z \\ & + J' \sum_{\langle \mathbf{r}\mathbf{r}' \rangle} (\mathbf{S}_{\mathbf{r},1} \cdot \mathbf{S}_{\mathbf{r}',2} + \mathbf{S}_{\mathbf{r},2} \cdot \mathbf{S}_{\mathbf{r}',1}), \end{aligned} \quad (1)$$

where $J > 0$ and $J' > 0$ are the intra- and interdimer exchange couplings, respectively, and H is the external magnetic field directed along the z axis. The vector \mathbf{r} labels the dimers located at the sites of a lattice with coordination number Z , and $\langle \dots \rangle$ denotes summation only over neighboring dimers. In (1) we have assumed that the couplings are unfrustrated so that each spin $\mathbf{S}_{\mathbf{r},\sigma}$ can be classified as belonging to one of the two sublattices (respectively, $\sigma = 1$ or $\sigma = 2$).

In the absence of impurities and external field and for sufficiently weak interdimer coupling $J' \ll J$ the system has a singlet ground state without any magnetic order, and a finite gap $\Delta \sim J$ to the lowest excitation which

is a triplet; known examples of materials exhibiting this type of ground state are KCuCl_3 [19] and TiCuCl_3 [20]. If the 3D coupling J' exceeds some critical value (typically of the order of J/Z), long-range Néel order appears; this situation is realized e.g. in NH_4CuCl_3 [21]. An external magnetic field closes the gap at the critical field $H = H_c = \Delta$, inducing a phase transition. At $H > H_c$ a finite magnetization along the field direction appears, accompanied by a staggered order in the plane perpendicular to the field; the $U(1)$ symmetry in the xy plane is spontaneously broken. This transition may be viewed as the Bose-Einstein condensation of magnons [15].

The presence of non-magnetic impurities drastically changes the above picture [1, 4, 10]. Impurities generate unpaired spins, which develop an effective interaction with each other mediated by the intact dimers between them. According to the Lieb-Schulz-Mattis theorem, the interaction between two unpaired spins is antiferromagnetic if they belong to the same sublattice and ferromagnetic otherwise, so in total the unpaired spins encourage an antiferromagnetic ordering which at $T = 0$ occurs at any arbitrarily small concentration of impurities c . Unpaired spins thus form a separate subsystem with the energy scale for its dynamics set by the average effective interaction $\tilde{J} \ll \Delta$. The excitation spectrum of the impure system is determined by the gapless continuum of the low-lying states resulting from the ordered unpaired-spin subsystem; this continuum coexists with the states above the spin gap Δ of the pure system which survive with reduced weight.

So, taken *separately*, both doping with non-magnetic impurities and application of an external field tend to induce ordering in a gapped spin system. The aim of the present Letter is to show that application of an external field to a doped system may drive it back into the disordered phase, causing reentrant behavior of the Néel order as a function of H . The qualitative form of the $T = 0$ phase diagram in the (H, J') space will be obtained from a mean-field treatment of the interaction between the dimer and unpaired spin subsystems.

Dynamics of an intact dimer system.— To derive the effective interaction between two unpaired spins, we have

to consider the dynamics of the pure dimer system first. For this purpose we use the dimer field theory [22] which may be viewed as a continuum version of the bond boson operator approach [17]. The quantum state is formulated as the product of dimer states of the form

$$|\psi\rangle = (1 - A^2 - B^2)^{1/2} |s\rangle + \sum_j (A_j + iB_j) |t_j\rangle, \quad (2)$$

where $|s\rangle$ denotes the singlet state and $|t_j\rangle$, $j = x, y, z$ are the three triplet states of the spin dimer in the Cartesian basis. The vectors \mathbf{A} , \mathbf{B} are connected with the magnetization $\mathbf{M} = \langle \mathbf{S}_1 + \mathbf{S}_2 \rangle$ and sublattice magnetization $\mathbf{L} = \langle \mathbf{S}_1 - \mathbf{S}_2 \rangle$ of the spin dimer as follows:

$$\mathbf{M} = 2(\mathbf{A} \times \mathbf{B}), \quad \mathbf{L} = 2(1 - A^2 - B^2)^{1/2} \mathbf{A}. \quad (3)$$

The Lagrangian density (per dimer) can be written as

$$\mathcal{L} = 2\hbar \mathbf{B} \cdot \frac{\partial \mathbf{A}}{\partial t} - E_{\text{dim}} - \frac{ZJ'}{4} \{(\nabla \mathbf{L})^2 + (\nabla \mathbf{M})^2\}$$

$$E_{\text{dim}} = J(A^2 + B^2) + \frac{ZJ'}{4} (\mathbf{M}^2 - \mathbf{L}^2) - H M_z, \quad (4)$$

where we use the notation $(\nabla \mathbf{A})^2 \equiv \sum_i (\partial \mathbf{A} / \partial x_i)^2$. Assuming $A, B \ll 1$, at the quadratic level one easily obtains the dispersion of a magnon with $S^z = \mu$ as $\varepsilon(\mathbf{k}) = \Delta(1 + k^2 \xi^2)^{1/2} - \mu H$, where

$$\Delta = [J(J - ZJ')]^{1/2}, \quad \xi = \frac{v}{\Delta}, \quad v = \left(\frac{ZJ'}{2} \right)^{1/2}. \quad (5)$$

Here ξ is the spin correlation length, $\xi \ll 1$ if the 3D interaction is small and $ZJ' \ll J$ (the lattice constant is set to unity).

Interactions between unpaired spins.— The effective interaction between two unpaired spins can be estimated [1] in second-order perturbation theory,

$$J_{\text{eff}} = \mathcal{K} \int d^3k \frac{(ZJ')^2}{\varepsilon(k)} e^{i\mathbf{k} \cdot \mathbf{r}} = \frac{4\pi \mathcal{K} (ZJ')^2}{rv\xi} K_1\left(\frac{r}{\xi}\right), \quad (6)$$

where \mathcal{K} is an unknown constant of the order of unity, determined by the matrix elements of the perturbation, \mathbf{r} is the vector connecting the two spins, K_1 is the MacDonald function, and we omit the oscillating sign depending on whether or not the spins belong to the same sublattice; we have used the $H = 0$ expression for the magnon energy since, as will be clear below, we are interested in fields which are small comparing to the gap Δ . If $r = 1$, there is an additional direct (first-order in the perturbation J') interaction between the spins. Since $\xi \ll 1$, one can write down the effective interaction as

$$J_{\text{eff}}(r) = J_0 \delta_{r,1} + J_1 r^{-3/2} e^{-r/\xi}, \quad (7)$$

where $J_0 \sim J'$ and $J_1 = (2\sqrt{2}\pi)^{3/2} \mathcal{K} J' (Z^5 J' / J)^{1/4}$. Since J_{eff} is decaying very fast with increasing r , it is sufficient to take into account interactions only between

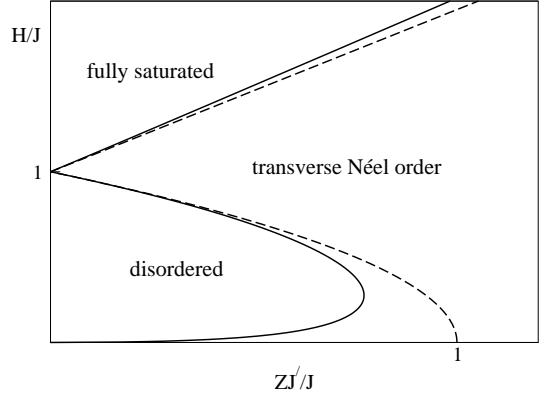


FIG. 1: A schematic mean-field $T = 0$ phase diagram of the model (1). The dashed line corresponds to a pure system and the solid line to a finite concentration of impurities. The boundaries of the disordered and saturated phases are determined by (13) and (14), respectively.

those unpaired spins which are nearest neighbors. For a given impurity concentration c , the distribution of distances R from an impurity to its nearest neighbor can be estimated in the continuum approximation (i.e. neglecting the presence of the lattice) as

$$p(R) = c \exp\left\{-\frac{4\pi c}{3} R^3\right\}, \quad \int p(R) 4\pi R^2 dR = 1. \quad (8)$$

The distribution of effective exchange couplings \tilde{J} between the neighboring unpaired spins is given by

$$P(\tilde{J}) = \sum_{\mathbf{R}} p(R) \delta(\tilde{J} - J_{\text{eff}}(R)).$$

Replacing the sum by an integral and substituting the exact value of $p(1) = Zc$, one obtains

$$P(\tilde{J}) = Zc\delta(\tilde{J} - J_0) + P_{\text{reg}}(\tilde{J}), \quad (9)$$

$$P_{\text{reg}}(\tilde{J}) = \Theta(J_1 e^{-1/\xi} - \tilde{J}) \frac{4\pi c \xi}{\tilde{J}} R_1^2 \exp\{-4\pi c R_1^3/3\},$$

where $R_1 \simeq \xi \ln(J_1/\tilde{J})$ and Θ is the Heaviside function; note that $P(\tilde{J})$ has an upper cutoff. The peak of the regular part P_{reg} occurs at $\tilde{J} = \tilde{J}_{\text{peak}} \simeq J_1 \exp\{-(4\pi c \xi^3)^{-1/2}\}$, and the “regular average” is

$$\langle \tilde{J} \rangle_{\text{reg}} = \int J P_{\text{reg}}(J) dJ \simeq 4\pi c \xi J_1 e^{-1/\xi} \gg \tilde{J}_{\text{peak}}. \quad (10)$$

The interacting system of unpaired spins and intact dimers.— We go on to study the static properties (e.g. the sublattice magnetization) of the impure system in a magnetic field in a mean-field approximation by minimizing the full energy $E = E_{\text{dim}} + E_{\text{unp}} + E_{\text{int}}$. Here, E_{dim} is the energy of the intact dimers, Eq. (4), E_{unp} is the energy of the subsystem of unpaired spins and E_{int} the interaction energy between the unpaired spins and the

intact dimer subsystem. The unpaired spin subsystem is ordered, and we therefore describe it as a two-sublattice antiferromagnet. Denoting the angle between the sublattice magnetization and the z axis as θ and the average spin length of an unpaired spin as s , we write the interaction energy (per dimer) as

$$E_{\text{int}} = cZJ's(M_z \cos \theta - L_x \sin \theta), \quad (11)$$

where the x axis is chosen along the direction of the staggered order. In the self-energy E_{unp} of the unpaired spin subsystem we include, for each unpaired spin, the interaction with nearest unpaired neighbors only; this gives

$$E_{\text{unp}} = 2c(-\frac{1}{2}Z_i\tilde{J}s^2\sin^2\theta - Hs\cos\theta). \quad (12)$$

Here Z_i is some number which has the sense of an average number of “nearest neighbors” for a fictitious random lattice formed by unpaired spins, and the energy is again taken per dimer, hence the factor $2c$ in front. The number Z_i can be safely put to 1, as the following estimate shows: We would like to know how many unpaired spins in the closest vicinity of a given one (which we put at the origin) can have “almost the same” effective interaction J_{eff} with it. Since J_{eff} decays as $e^{-r/\xi}$, we have to count impurities in a spheric layer with some radius R (the distance to the closest impurity, on average $R \sim c^{-1/3}$) and thickness $h \sim \xi$. Thus the average number of other unpaired spins which are at the same distance from the origin as the closest one is $4\pi R^2\xi c \ll 1$, so $Z_i \simeq 1 + 4\pi cR^2\xi \simeq 1$.

We now derive from the mean-field approach the static properties for fixed effective interaction \tilde{J} and afterwards perform an averaging over \tilde{J} . It is convenient to parameterize the vectors \mathbf{A} and \mathbf{B} as follows:

$$\mathbf{A} = \{\sin \alpha \cos \gamma, 0, 0\}, \quad \mathbf{B} = \{0, \sin \alpha \sin \gamma, 0\}.$$

It is easy to see that $\alpha = 0, \theta = 0$ is always an extremum of E describing a state with a fully polarized unpaired spin subsystem and a non-magnetic (singlet) dimer subsystem. A trivial analysis yields the following equation for the stability boundary of this solution:

$$(H^2 - J^2)(H - \tilde{J}s) + cs(ZJ')^2(J + csH - cs^2\tilde{J}) + ZJ'(H - \tilde{J}s)(J - 2csH) = 0. \quad (13)$$

Another obvious solution is the saturated state with all spins fully polarized, which corresponds to $\theta = 0, \alpha = \pi/2, \gamma = \pi/4$. This state becomes unstable if the field drops below the saturation value

$$H_s = J + ZJ'(1 + cs). \quad (14)$$

At fixed J' the equation (13) has two solutions for H . Up to the second order in J' , \tilde{J} and to the first order in c the lower and upper critical fields are given by

$$H_{c1} \simeq \tilde{J}s + cs(ZJ')^2/J, \quad (15)$$

$$H_{c2} \simeq J - ZJ'(1/2 - cs) - (ZJ')^2/(4J). \quad (16)$$

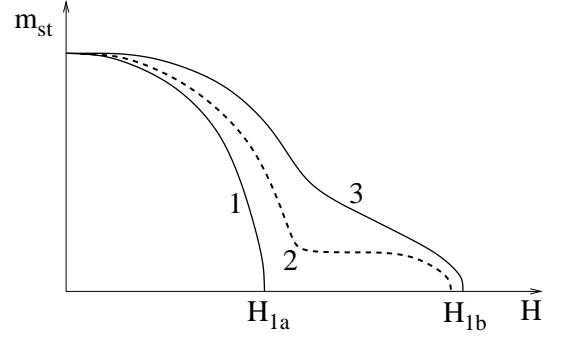


FIG. 2: Schematic behavior of the staggered magnetization as function of the field H . Curves 1, 2, and 3 correspond to the regimes $\alpha \ll x_1$, $x_1 \ll \alpha \ll x_2$, and $\alpha \gg x_2$, respectively, $\alpha = ZJ'/(2J)$ and $x_{1,2}$ as in (21), (22).

It is easy to obtain the behavior of α, θ, γ in the vicinity of the lower critical field H_{c1} :

$$\begin{aligned} \theta &\simeq [2(1 - H/H_{c1})]^{1/2}, \quad \alpha \simeq csZJ'\theta \cos \gamma, \\ \gamma &\simeq (\tilde{J} - cZJ')s/2. \end{aligned} \quad (17)$$

The total staggered magnetization per dimer in the vicinity of H_{c1} vanishes as a square root:

$$m_{\text{st}} \simeq cs(1 + ZJ'/J)[8(1 - H/H_{c1})]^{1/2}, \quad (18)$$

where the term proportional to J' describes the contribution of intact dimers. Thus, the following physical picture emerges: At zero external field, the presence of impurities induces a finite staggered order, $\alpha \neq 0$. When the external field H is switched on, it induces canting of spins in the field direction, i.e. θ starts to deviate from $\pi/2$. However, with increasing H the canting angle θ moves towards 0, diminishing the effective staggered field from the unpaired spins acting on the dimer subsystem. Unpaired spins become saturated at $H = H_{c1}$ (θ becomes zero), and simultaneously the staggered order in the dimer subsystem vanishes (α becomes zero). The system enters a disordered phase where the dimers are in a singlet state and unpaired spins are fully magnetized. The resulting phase diagram is sketched in Fig. 1.

As a byproduct of this description, one can study how the high-energy spectrum (above the gap Δ) is affected by presence of impurities. One may replace E_{dim} in the Lagrangian (4) by the full energy E and assume that θ is frozen at its equilibrium value. This amounts to neglecting the dynamics of the unpaired spin subsystem which occurs at a much lower energy scale \tilde{J} , justifying to take into account only the static part described by a fixed θ . In that way, one obtains that the triplet gap splits due to the appearance of the staggered order in the x direction; at $H = 0$, the gaps are related to the order parameter $A_0 \propto m_{\text{st}}$ as follows:

$$\Delta_{y,z} = (\Delta^2 + 4v^2 A_0^2)^{1/2}, \quad \Delta_x = (\Delta^2 + 12v^2 A_0^2)^{1/2}. \quad (19)$$

For $A_0 \ll 1$, the square of the order parameter determining the intensity of the Bragg peak is approximately linearly related to the gap energy. This proportionality between the change in the gap energy and the intensity of the Bragg peak was observed experimentally in TiCuCl_3 doped with Mg [14] by varying the temperature. Our calculation is for $T = 0$, but we believe that this relation continues to be valid for finite temperature as well.

Averaging over the impurity distribution.— As final step we have to average the staggered magnetization (18) with H_{c1} given by (15), using the distribution function (9). Formally, the field H_0 at which m_{st} completely disappears is determined by the upper cutoff of $P(\tilde{J})$. However, the singular (δ -function) part of $P(\tilde{J})$ has to be neglected for two reasons: (a) it has a small weight of Zc , so that the corresponding contribution to m_{st} is of the order of c^2 ; (b) it describes unpaired spins located at neighboring sites, and they will have a strong tendency to build a singlet state since their interaction with each other is much stronger than with the rest of the unpaired spin “network”. The regular part P_{reg} of the distribution carries the main weight $1 - Zc$ and corresponds to much smaller \tilde{J} with the cutoff at $\tilde{J} = J_1 e^{-1/\xi}$. Its contribution to m_{st} vanishes above the characteristic field

$$H_1 = sJ_1 e^{-1/\xi} + cs(ZJ')^2/J \quad (20)$$

One has to distinguish two different regimes, depending on the strength of the interdimer interaction. For a very small interdimer coupling

$$\frac{ZJ'}{J} \ll 2x_1, \quad \text{where} \quad x_1^{3/4} e^{1/\sqrt{x_1}} = (2\pi)^{3/2} \frac{\mathcal{K}}{c}, \quad (21)$$

the second term in (20) is always leading, and

$$H_1 \simeq H_{1a} = cs(ZJ')^2/J,$$

with m_{st} behaving as a pure square root $\sqrt{H_{1a} - H}$. For stronger J' the inequality (21) is violated, then the first term in (20) becomes leading, and

$$H_1 \simeq H_{1b} = sJ_1 e^{-1/\xi}.$$

The behavior of m_{st} for $H < H_1$ depends again on the interdimer interaction strength. If $\langle J \rangle_{\text{reg}} \ll c(ZJ')^2/J$, which corresponds to weak interdimer coupling $ZJ'/J \ll 2x_2$ with $x_2 \gg x_1$ given by

$$x_2^{1/4} \exp\{x_2^{-1/2}\} = 2(2\pi)^{5/2} \mathcal{K}, \quad (22)$$

then the main contribution to the staggered magnetization m_{st} has an overall $\sqrt{H_{1a} - H}$ behavior, and additionally there is a weak shoulder extending to a higher field $H = H_{1b}$. The shoulder strength grows with increasing J' and for $2x_2 \ll ZJ'/J \ll 1$ merges with the main part, as sketched in Fig. 2.

In summary, we have shown that in a system of weakly coupled spin dimers doped with non-magnetic impurities,

the application of an external field H may lead to a reentrant behavior of long-range antiferromagnetic order as a function of field. From the phase diagram of Fig. 1 it is clear that this phenomenon is most likely to occur in materials with a sufficiently small ratio of inter- to intradimer exchange. Therefore, among known materials, KCuCl_3 is the most promising candidate.

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